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COMPLETE SPECIFICATION.

Interpolymers of Ethylene.

We, MONSANTO CHEMICAL COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to low molecular weight interpolymers of ethylene and vinyloxyethanol (vinyl β-hydroxyethyl ether, $CH_2=CH.O.CH_2CH_2OH$) having low coefficients of friction.

The present invention provides an interpolymer of ethylene and vinyloxyethanol which may contain a small amount of another copolymerisable vinyl monomer, said interpolymer having a molecular weight of less than 5,000 as determined from freezing point depression data obtained in dilute solution in benzene.

The interpolymers of the present invention have a low coefficient of friction, more especially coefficients less than 0.130 dynes/cm² as measured by a Kyropoulos four-ball pendulum. As a rule they have a weight percentage of vinyloxyethanol units in the interpolymer of between 20% and 70%. Those interpolymers having from 30% to 60% by weight of vinyloxyethanol units in the molecule have coefficients of friction below 0.115 dynes/cm². The optimum coefficients of friction are found with those copolymers having 35% to 50% by weight of vinyloxyethanol units. To a marked extent in the low molecular weight interpolymer of the invention, the coefficient of friction is independent of the molecular weight. It is nevertheless desirable to use products having particular ranges of molecular weight for functional fluids and as plasticisers in order to have proper viscosities and other properties; in all cases molecular weights below 5,000 are required.

The preferred interpolymers of the present invention are oils which have molecular weights of from 100 to 2,000, more especially from 200 to 1,500; but interpolymers which are greases or soft waxes and which usually have molecular weights of from 2,000 up to 5,000 are of value as lubricants and functional fluids, although in more limited applications and under conditions in which they are liquid, and are regarded as within the scope of the present invention. The aforesaid molecular weights are the number average molecular weights calculated from freezing point depression data obtained in dilute benzene solution in a standard Beckmann apparatus. The physical form of the ethylene-vinyloxyethanol interpolymers varies to some extent with the proportions of the monomers present therein, with the purity of the interpolymer and with possible crystallinity effects, but it varies from an oil to a wax within the molecular weight ranges noted above, and continues to change until hard waxes are obtained having molecular weights of from 5,000 to

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10,000. At molecular weights above 10,000, the ethylene-vinyloxyethanol interpolymers are true high molecular weight polymers having the typical tensile strengths and other properties of such polymers; the molecular weights thereof are the number average molecular weights as calculated from viscosity in solution.

While, within limits, the lubricity of the interpolymers of the present invention is independent of their molecular weight, it will be recognised that for most functional fluid and lubrication uses the interpolymers require to be pumpable liquids under the conditions of use; and for most applications the interpolymers must have kinematic viscosities between 5 and 10,000 centistokes at 100° F., preferably from 20 to 5,000 centistokes at 100° F. At higher temperatures, the kinematic viscosities are generally lower, e.g. from 2 to 500 centistokes at 210 F., although higher viscosity material can be used at higher temperatures.

The viscosity index of the low molecular weight ethylene-vinyloxyethanol interpolymers of the present invention is, in general, approximately equivalent to that of a good grade of solvent-refined mid-continent lube oil stock, i.e., from 90 to 100 (ASTM D 576-41). However, the viscosity index will vary to some extent with molecular weight, with the proportions of the monomers, and be from about 70 to 110.

The low molecular weight interpolymers of the present invention are conveniently prepared by the free radical-catalysed interpolymerisation of ethylene and vinyloxyethanol at any pressure below 10,000 p.s.i. gauge, e.g., pressures from 1,000 up to 8,000 p.s.i. or even higher; pressures of approximately 5,000 p.s.i. are particularly suitable. While the molecular weight of the interpolymers is conveniently controlled by regulation of the pressure at which polymerisation is carried out, the desired low molecular weight interpolymers may be obtained by appropriate variation of other conditions of polymerisation.

The production of the low molecular weight ethylene-vinyloxyethanol interpolymers is normally carried out under conditions suitable for the high pressure polymerisation of ethylene, except for the use of the lower pressures indicated above. The polymerisation is generally effected at temperatures of from 50 to 250° C., preferably at from 100 to 200° C. Higher temperatures may be employed so long as they do not cause pyrolysis or unduly rapid reaction; it is also possible to employ lower temperatures, even as low as room temperature; however, the reaction is not very rapid at such low temperatures. Moreover, when catalysts which dissociate to liberate free radicals in the polymerisation reaction are employed, it is desirable to employ temperatures high enough to cause such dissociation.

It is known that ethylene will polymerise at elevated temperature and pressure in the absence of catalysts, especially if it contains trace amounts of oxygen which have a catalytic effect. However, in preparing the interpolymers of the present invention, it is preferred to employ a free radical-initiating catalyst to ensure the preparation of the polymers in reasonable reaction times. In general, catalysts used for polymerising ethylene, including oxygen, are suitable. On a weight basis, 10 to 200 parts of oxygen per million parts of monomers is very suitable. Among the preferred catalysts are the peroxide and azo catalysts. The peroxide catalysts include ditolyl peroxide, benzoyl peroxide, diacetone peroxide, succinyl peroxide, acetyl peroxide, acetylbenzoyl peroxide, metabromobenzoyl peroxide, lauroyl peroxide, 2,2-bis-tertiary-butylperoxybutane, hydrogen peroxide, zinc peroxide, peracetic acid and the alkali metal and ammonium persulphates, perborates and percarbonates. In general, all these peroxide compounds which are either formed by the action of hydrogen peroxide on ordinary acids or which give rise to hydrogen peroxide on treatment with dilute sulphuric acid may be used. The azo catalysts include bis-benzene diazosuccinate, the inorganic acid salts of 2,2¹-diguanyl-2,2¹-azopropane, 2,2¹-azobis(methyl-isobutyrate) and 2,2¹-azobis(isobutyramide). The catalyst is preferably used in the least quantity which will produce the desired polymer in a reasonable reaction time. The amount of catalyst has some effect upon the molecular weight since larger amounts of catalyst ordinarily lead to the production of the lower molecular weight polymers. However, the amount of catalyst employed is usually from 0.0005% to 2% by weight, based on the monomers. Small amounts of other copolymerisable vinyl monomers, e.g. up to 15% by weight of vinyl acetate may be polymerised together with the ethylene and vinyloxyethanol.

The vinyloxyethanol used in the examples was produced by the method disclosed in U.S. Patent No. 1,959,927: another method which may be used is that of British Patent No. 398,173 and U.S. Patent No. 2,097,590.

The following examples illustrate the nature of the invention and the manner in which it may be performed.

EXAMPLE 1.

To a jacketed tubular reactor, the jacket of which is maintained at 180 C., ethylene

and vinyloxyethanol were continuously charged in substantially equal proportions by weight together with 0.2% by weight of ditertiarybutyl peroxide and polymerised at a pressure of 5,000 p.s.i. The maximum temperature in the reactor was 200° C. The conversion to copolymer was more than 20%.

The interpolymer thus obtained was treated with a large volume of hot acetone to dissolve it and the solution filtered to remove insoluble material. The acetone was then evaporated from the acetone-soluble portion of the interpolymer, which was characterised as follows:—

Weight % Hydroxyl	8.23
Weight % Vinyloxyethanol ...	42.6
Gardner-Holt Viscosity (Stokes)	32
Pour Point, °F.	28
Specific Viscosity (measured at 25° C. on a 5% solution in pyridine)	0.28

The coefficient of friction was determined by a Kyropoulos pendulum modified with a 4-ball contact (see "A Convenient Measurement of Friction Coefficient", by H. E. Malincke, Lubrication Engineering, March-April, 1956). Polished steel balls were used as the contacts in the test. The ethylene-vinyloxyethanol interpolymer proved to have a very low coefficient of friction, 0.106 dynes/cm². This compares very favourably with the values for well known lubricants, e.g., 0.187 for mineral oil, 0.200 for gylcerine, 0.232 for ethylene glycol, and 0.143 for a commercial polyglycol synthetic lubricant. The ethylene-vinyloxyethanol interpolymer exhibited good temperature stability as shown by its slight change in viscosity when it was maintained at 100—150° C. for several days.

EXAMPLE 2.

An interpolymer was prepared which had approximately the same proportions of monomers as that of Example 1, but a slightly higher molecular weight; the weight percentage of vinyloxyethanol was 42.5%, but the viscosity in solution (5% in pyridine) was 0.302 compared with 0.280 for the interpolymer of Example 1. The coefficient of friction, determined as described in Example 1, was 0.105, or almost exactly that of the interpolymer of Example 1. This indicates that small changes in the molecular weight of the low molecular weight interpolymers have no appreciable effect on the coefficient of friction. The interpolymer had a kinematic viscosity of 2124.8 centistokes at 100° F. or 74.7 centistokes at 210° F., and a viscosity index of 95.3 (ASTM D 576—41).

EXAMPLE 3.

Ethylene and vinyloxyethanol were copolymerised in a charge in the proportions of 1 to 3 by weight, utilising 1% by weight of ditertiarybutyl peroxide as catalyst. The pressure was 5,000 p.s.i., the jacket temperature 165—170° C., and the maximum internal temperature 185° C.; a good conversion was obtained.

The interpolymer was characterised as follows:—

Weight % Hydroxyl	11.59
Weight % Vinyloxyethanol ...	60.1
Gardner-Holt Viscosity (Stokes)	90
Pour Point, °F.	0
Specific Viscosity (measured at 25° C. on a 5% solution in pyridine)	0.28

The coefficient of friction was 0.115 dynes/cm², the kinematic viscosity was 4977.9 centistokes at 100° F., or 129.3 centistokes at 210° F., and the viscosity index was 98.7. This interpolymer has a molecular weight of about 960 as determined from freezing point data.

EXAMPLE 4.

Ethylene, 60 parts, and vinyloxyethanol, 20 parts, were interpolymerised in the presence of 20 parts of acetone, all parts being by weight. Ditertiarybutyl peroxide, 0.5%, was employed as an initiator and the polymerisation conditions were substantially those employed in Example 1.

The acetone-soluble portion of the interpolymer oil was characterised as follows:

Weight % of Hydroxyl	4.68
Weight % Vinyloxyethanol ...	24.3
Gardner-Holt Viscosity (Stokes)	5
Pour Point, °F.	20
Specific Viscosity (measured at 25° C. on a 5% solution in pyridine)	0.195

The coefficient of friction was 0.122 dynes/cm², the kinematic viscosity 218.7 centistokes at 100° F. or 16.83 centistokes at 210° F. and the viscosity index was 87.7.

A low molecular weight ethylene-vinylethanol interpolymer oil having a vinyloxyethanol content of substantially 13% by weight had a coefficient of friction of 0.138 dynes/cm², as determined by the method employed in the above examples whilst a low molecular weight homopolymer of vinyloxyethanol had a coefficient of friction of 0.146 dynes/cm².

Several samples of ethylene-vinyloxyethanol copolymers were tested for anti-wear properties by the Shell 4-Ball Wear Test (600 r.p.m., 10 kilogram weight, 167° F., for one hour, 52—100 steel-on-steel).

The ethylene-vinyloxyethanol copolymer having a 42.5% vinyloxyethanol unit content had very good antiwear properties as shown by a scar diameter of only 0.27 mm. This compares very favourably with such values as 0.41 mm. for ethylene glycol, 0.48 mm. for white oil, 0.61 mm. for paraffin oil, and 0.45 mm. for tricresyl phosphate. An ethylene-vinyloxyethanol copolymer having a 60% by weight vinyloxyethanol unit content had a value of 0.29 mm., and one having a 24.7% by weight vinyloxyethanol unit content also had a value below the 0.50 mm. value used as a criterion of antiwear properties.

While the friction tests reported above were made utilising polished steel as contact, which metal is recognised as standard for testing lubricants, the results obtained may be considered representative with reasonable accuracy of those obtainable with other metals such as other steels, irons, ferrous metals in general, polished chromes, aluminiums, brasses, bronzes and coppers.

The low coefficients of friction shown by the interpolymers of this invention indicate various uses as lubricants. They may be used to lubricate metal bearings or in any other applications requiring ferrous metals to be coated with lubricating films or in which a film of the interpolymers separates metal surfaces in close juxtaposition with each other, particularly when there is relative movement between the surfaces. They are also useful as functional fluids, e.g., as automotive hydraulic brake fluids and as power transmission fluids. In many lubrication and functional fluid applications they may be used in compositions together with other materials useful in such applications, e.g., together with mineral oils.

The low molecular weight liquid and waxy ethylene-vinyloxyethanol interpolymers may also be used as leather softeners; the polymers also make leather water-repellant and more receptive to stains and polishes. Leathers may be impregnated by brushing or rubbing the polymers into the leather, or by permitting the liquid polymers to soak into the leather.

It will be realised that the molecular weight values and percentages of monomer values in the copolymers as described herein represent averages. Fractionation of the copolymers into fractions soluble in acetone or hexane or neither tends to narrow the molecular weight and differences in composition. It is believed that the acetone-soluble fractions used in the test procedures described herein have fairly narrow molecular weight ranges and compositional distributions. The interpolymers have the desired properties regardless of their method of isolation.

WHAT WE CLAIM IS:—

1. An interpolymer of ethylene and vinyloxyethanol which may contain a small amount of another copolymerisable vinyl monomer, said polymer having a molecular weight of less than 5,000 as determined from freezing point depression data obtained in dilute solution in benzene.

2. An interpolymer of ethylene and vinyloxyethanol containing not more than 15% by weight of other ethylenically unsaturated monomers copolymerisable therewith, said interpolymer having a molecular weight of less than 5,000 as determined from freezing point depression data obtained in dilute solution in benzene.

3. An interpolymer according to Claim 2 having a kinematic viscosity of 5 to 10,000 centistokes at 100° F.

4. An interpolymer according to either of Claims 2 or 3 having a kinematic viscosity of 20 to 5,000 centistokes at 100° F.

5. An interpolymer according to any of Claims 2 to 4 having a coefficient of friction below 0.115 dynes/cm² as measured by a Kyropoulos four-ball pendulum.

6. An interpolymer according to any of the preceding claims having a molecular weight of 200 to 1,500.

7. A process for the production of an interpolymer of ethylene and vinyloxyethanol containing not more than 15% by weight of other ethylenically unsaturated monomers copolymerisable therewith according to Claim 2 which comprises polymerising a mixture of ethylene and vinyloxyethanol, with or without not more than 15% by weight of other ethylenically unsaturated monomers copolymerisable therewith at a pressure below 10,000 p.s.i. in the presence of oxygen or a free radical initiating catalyst.

8. A process according to Claim 7 in which the reaction is carried out at 50 to 250° C.

9. A process according to Claim 8 in which the reaction is carried out at 100 to 200° C.

10. A process for the production of an interpolymer according to Claim 7 and substantially as hereinbefore described with reference to any of the examples.

11. A lubricant comprising an interpolymer according to any of Claims 1 to 6.

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